

# A New Copper Coordination Polymer with Magnetic Property Based on 3-(1,2,4-Triazol-1-yl)benzoic Acid<sup>①</sup>

ZHANG Heng-Da<sup>1,2</sup>(张亨达) WANG Shuai-Hua<sup>1</sup>(王帅华) WU Shao-Fan<sup>1②</sup>(吴少凡)

<sup>1</sup>(Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China); <sup>2</sup>(University of Chinese

Academy of Sciences, Beijing 100039, China)

**ABSTRACT** A copper coordination polymer, namely  $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  **1** ( $\text{HL} = 3\text{-}(1,2,4\text{-triazol-1-yl})\text{benzoic acid}$ ) has been synthesized by the hydrothermal reaction under 140 °C. The structure of **1** was characterized by single-crystal X-ray diffraction analysis, elemental analyses, powder X-ray diffraction, IR spectroscopy, and thermogravimetric analysis. Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in  $P2_1/n$  space group with  $a = 12.374(5)$ ,  $b = 12.730(5)$ ,  $c = 12.561(5)$  Å,  $\beta = 91.105(9)$  °,  $V = 1978.2(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.618$  g/cm<sup>3</sup>,  $\mu = 1.160$  mm<sup>-1</sup>,  $F(000) = 964$ , the final  $R = 0.0449$  and  $wR = 0.1443$  with  $I > 2\sigma(I)$ . Magnetic measurements show that **1** exhibits antiferromagnetic interactions by the analysis of magnetic test data.

**Keywords:** copper coordination polymer; hydrothermal reaction; crystal structure, magnetic property

**DOI:** 10.14102/j.cnki.0254-5861.2011-1615

## 1 INTRODUCTION

In recent years, coordination polymers have attracted considerable attention due to their potential applications such as luminescence, gas adsorption, gas capture and separations, chemical catalysis, magnetic behavior, electrical conductivity, drug delivery, and so on<sup>[1-7]</sup>. Varieties of coordination polymers have been synthesized with more interesting structures and desired functions, which have well-defined and

Received 28 February 2017; accepted 25 April 2017 (CCDC 1534790)

① The work was supported by the National Natural Science Foundation of China (No. 21601186), the Natural Key R&D Program of China (No. 2016YFB0701004) and Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB20000000)  
② Corresponding author. E-mail: wsf@fjirsm.ac.cn

designable structures through selecting metal ions and ligands on purpose<sup>[8-12]</sup>. Most of them were synthesized by means of self-assembly approach with inorganic and organic building units<sup>[13]</sup>. In this process, the major task is how to choose appropriate metal-connecting nodes and bridging ligands to obtain desired structures and functions<sup>[14]</sup>. Among organic ligands, multidentate N and O-donor bridging ligands with multicarboxylate are often selected as multifunctional organic linkers<sup>[15-17]</sup>, which construct novel frameworks due to their abundant coordination modes to metal ions, allowing for various structural topologies, and their ability to act as H-bond acceptors and donors.

In this study, a multidentate organic linker 3-(1,2,4-triazol-1-yl)benzoic acid (HL) and Cu<sup>2+</sup> ions were selected to synthesize novel coordination polymers with interesting magnetic properties. A new 2D supramolecular coordination polymer [CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · H<sub>2</sub>O **1** has been successfully synthesized by hydrothermal synthesis. The structure of **1** has been comprehensively investigated by single-crystal analysis and various tests. Meanwhile, magnetic measurements demonstrate that **1** shows antiferromagnetic interactions.

## 2 EXPERIMENTAL

### 2.1 Materials and instruments

All reagents were commercially available and used as received without further purification. Powder X-ray diffraction (PXRD) patterns at room temperature were collected on a Rigaku Miniflex II diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ) at 40 kV and 40 mA in the range of  $5 \leq 2\theta \leq 85^\circ$ . Simulated PXRD patterns were derived from the Mercury Version 1.4 software (<http://www.ccdc.cam.ac.uk/products/mercury>). The elemental analyses of C, H and N were performed on an Elementar Vario EL III micro-analyzer. Thermogravimetric analysis (TGA) experiments were done on a TGA/NETZSCH STA449F3 thermogravimetric analyzer in N<sub>2</sub> atmosphere with the sample heated in an Al<sub>2</sub>O<sub>3</sub> crucible at a heating rate of 10 K/min. The FT-IR spectra were obtained on a Perkin-Elmer Spectrum One Spectrometer using KBr pellets in the  $4000 \sim 400 \text{ cm}^{-1}$  range. Magnetic measurements were performed using a SQUID magnetometer (MPMS, Quantum Design) and a commercial Quantum Design Physical Property Measurement System (PPMS). Powder samples of [CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · H<sub>2</sub>O were placed in a gel capsule ample holder that was suspended in a plastic drinking straw. The magnetic susceptibility was measured at 0.1 T from 300 to 2 K (temperature scan of 5 K/min), and the magnetization was measured at 2

K with applied fields from -8 to 8 T (field scan of 0.1 T/step).

## 2. 2 Synthesis of $[\text{CuL}_2(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ (1)

The mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (90.60 mg, 0.38 mmol) and 3-(1,2,4-triazol-1-yl)benzoic acid (HL) (47 mg, 0.25 mmol) in 10.0 mL of distilled water was sealed into a 25 mL Teflon-lined stainless-steel vessel under autogenous pressure, and then heated to 140 °C, kept at this temperature for 2 days, and finally cooled to room temperature. Blue block crystals suitable for X-ray analyses were obtained, washed with distilled water and dried in air. Yield: 68% (based on Cu) for **1**. Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{CuN}_6\text{O}_7$  **1**: C, 43.77; H, 3.67; N, 17.02%. Found: C, 44.03; H, 3.71; N, 16.91%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3446 b, 3139 m, 3028 w, 1667 w, 1568 vs, 1527 s, 1444 w, 1392 vs, 1360 vs, 1283 s, 1215 s, 1148 vs, 1065 m, 987 s, 899 m, 831 w, 780 s, 728 w, 671 s, 603 w, 526 w, 485 w, 433 w.

## 2. 3 Structure determination

The single crystal of **1** was mounted on glass fibers with dimensions of 0.25mm × 0.10mm × 0.09mm. The single-crystal X-ray diffraction measurement was performed on a Saturn 724 CCD for **1** which was equipped with a graphite-monochromatic  $\text{MoK}\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ) by an  $\omega$  scan mode. The structure was solved by direct methods using the *SHELXS-97* version 5 package<sup>[18]</sup>. Subsequent successive differences Fourier syntheses yielded other non-hydrogen atoms. The final structures were refined using a full-matrix least-squares refinement on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of ligands were added geometrically and refined using the riding model. All calculations were carried out by the *SHELXL-97* program package of crystallographic software<sup>[19]</sup>. A total of 16660 reflections were collected and 4506 were independent ( $R_{\text{int}} = 0.0310$ ). All non-H atoms were refined anisotropically. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding mode on the attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The lattice water molecule is disordered over two positions with site occupancy factors of 0.54/0.46. The positions of hydrogen atoms attached to carbon atoms were generated geometrically. The title compound crystallizes in the monoclinic system, space group  $P2_1/n$ . Selected bond distances and bond angles for **1** are listed in Table 1, and hydrogen bonds are listed in Table 2.

## 3 RESULTS AND DISCUSSION

### 3. 1 Description of the crystal structure

Structural analyses reveal that **1** crystallizes in monoclinic space group  $P2_1/n$  and features a 1D framework constructed by  $L^-$  ligands, coordinated  $H_2O$  molecules and Cu(II) ions. There exist one Cu(II) atom, two  $L^-$  ligands, two coordinated  $H_2O$  molecules, and one lattice water molecule in an asymmetric unit (Fig. 1). All the crystallographically unique Cu(II) ions are six-coordinated in a distorted octahedral coordination geometry, and the Cu–O and Cu–N distances fall in the normal range of  $1.946(2)\sim2.647(2)$  Å, which is comparable to other relative reported compounds<sup>[20]</sup>. The adjacent Cu(II) atoms are bound together through  $L^-$  linker with the distance of  $8.901(2)$  Å, which results in negligible interaction between adjacent Cu(II) atoms. Two  $L^-$  ligands adopt their N and O atoms to chelate two Cu(II) atoms to form a dinuclear  $[Cu_2L_2]$  cluster and the  $[Cu_2L_2]$  clusters connect with each other to fabricate a 1D chained structure. The 2D supramolecular framework is constructed through hydrogen bonding interactions between adjacent 1D chains (dotted line of Fig. 2, hydrogen bonds of  $O(1W)-H(1WA)\cdots O(12)$ ,  $O(1W)-H(1WB)\cdots O(22)$ ,  $O(2W)-H(2WA)\cdots N(12)$ ,  $O(3W)-H(3WA)\cdots O(2W)$ ,  $O(3W)-H(3WA)\cdots O(2W)$ , and  $O(2W)-H(2WB)\cdots O(22)$ ), which shows  $\pi\cdots\pi$  interaction in the layer with the centroid-to-centroid distance of  $3.962(2)$  Å and vertical distance of  $3.768(2)$  Å.

### 3.2 Powder X-ray diffraction patterns and thermal stability

The thermogravimetric analysis (TGA) experiment shows that **1** has a weight loss of 10.6% up to  $170$  °C, in accord with the release of one lattice water molecule and two coordinate water molecules (calcd. 10.58%). No weight loss occurred until heating up to approximate  $260$  °C, indicating that **1** has high thermal stability (Fig. 3a), and the framework began to decompose when keeping heating. The PXRD measurement and elemental analysis affirm the phase purity of **1**. The experimental PXRD pattern of **1** is in good agreement with its simulated one from the single-crystal X-ray data, and when the temperature increased to  $100$  °C, the molecular framework of **1** remained stable, and continuous heating led to framework collapse, presumably due to decomposition of organic ligand (Fig. 3b). IR spectrum of the compound exhibits broad absorption centered at  $3446\text{ cm}^{-1}$ , which belongs to the O–H stretching vibrations of water molecules. The strong bands at  $1563$  and  $1526\text{ cm}^{-1}$ , and  $1390\text{ cm}^{-1}$  are characteristic of the asymmetric and symmetric stretching vibrations of carboxylate groups for the compound, respectively.

### 3.3 Magnetic properties of **1**

The variable-temperature magnetic susceptibilities of **1** were measured under  $1\text{ kOe}$  over the  $2\sim300$  K temperature range (Fig. 4a). The measured  $\chi_M T$  value at  $300$  K is  $0.756\text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ , which is higher than the expected spin-only value of  $0.375\text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$  for an isolated  $Cu^{2+}$  ion with  $g = 2.0$  (Fig. 5a)<sup>[21]</sup>.

Upon cooling, the  $\chi_M T$  value increases to a maximum of  $0.801 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 31 K, then the  $\chi_M T$  value decreases to a minimum of  $0.79 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 2 K. It indicates the existence of antiferromagnetic interaction in **1**. The magnetic susceptibility above 50 K follows well with the Curie-Weiss law. The fit of experimental data for the plot of  $\chi_M$  vs.  $T$  over the temperature range of 5~300 K yielded the Curie constant  $C = 0.795 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and Weiss constant  $\theta = -0.12 \text{ K}$ , suggesting antiferromagnetic interactions among Cu<sup>2+</sup> ions. Fig. 4b shows the field-dependent magnetization at 2 K to further confirm the magnetic interactions in **1**. The magnetization increases rapidly as the field is lifted from zero, and then slowly increases to  $0.92 \mu\text{B}$  at 800 kOe, which reaches the saturation value ( $1.0 \mu\text{B}$ ), supporting the antiferimagnetic ground state.

## 4 CONCLUSION

In summary, a new 2D supramolecular coordination polymer  $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  **1** has been successfully fabricated by hydrothermal synthesis. The single-crystal X-ray diffraction analysis, elemental analyses, powder X-ray diffraction, IR spectroscopy and thermogravimetric analysis have been used to investigate the structure of compound **1**. The 2D supramolecular framework is connected through the adjacent 1D chains via hydrogen bonding interactions. Magnetic measurements demonstrate that compound **1** shows interesting antiferromagnetic interactions. This work provides an effective way to construct new supramolecular coordination polymers and explore interesting properties using N and O-donor bridging ligands.

## REFERENCES

- (1) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science* **2002**, *295*, 469–472.
- (2) Gao, H. X.; Shreeve, J. M. Azole-based energetic salts. *Chem. Rev.* **2011**, *111*, 7377–7436.
- (3) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. Luminescent metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.
- (4) Hu, Z.; Deibert, B. J.; Li, J. Luminescent metal-organic frameworks for chemical sensing and explosive detection. *Chem. Soc. Rev.* **2014**, *43*, 5815–5840.
- (5) Lacroix, P. G.; Malfant, I.; Lepetit, C. Second-order nonlinear optics in coordination chemistry: an open door towards multi-functional materials and molecular switches. *Coord. Chem. Rev.* **2016**, *308*, 381–394.
- (6) Frérey, G. Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **2008**, *37*, 191–214.
- (7) Furman, J. D.; Warner, A. Y.; Teat, S. J.; Mikhailovsky, A. A.; Cheetham, A. K. Tunable, ligand-based emission from inorganic-organic frameworks: a new approach to phosphors for solid state lighting and other applications. *Chem. Mater.* **2010**, *22*, 2255–2260.
- (8) Shekhah, O.; Liu, J.; Fischer R. A.; Wöll, C. MOF thin films: existing and future applications. *Chem. Soc. Rev.* **2011**, *40*, 1081–1106.

- (9) Furukawa, H.; Cordova, K. E.; O'Keeffe M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, 1230444.
- (10) Slater, A.; Cooper, A. Function-led design of new porous materials. *Science* **2015**, *348*, 988–997.
- (11) Osawa, M.; Hoshino, M.; Hashimoto, M.; Kawata, I.; Igawa, S.; Yashima, M. Application of three-coordinate copper(I) complexes with halide ligands in organic light-emitting diodes that exhibit delayed fluorescence. *Dalton Trans.* **2015**, *44*, 8369–8378.
- (12) Lazari, G.; Stamatatos, T. C.; Raptopoulou, C. P.; Pscharis, V.; Pissas, M.; Perlepes S. P.; Boudalis A. K. A metamagnetic 2D copper(II)-azide complex with 1D ferromagnetism and a hysteretic spin-flop transition. *Dalton Trans.* **2009**, *3215–3221*.
- (13) Chen, B. L.; Xiang, S. C.; Qian, G. D. Metal-organic frameworks with functional pores for recognition of small molecules. *Acc. Chem. Res.* **2010**, *43*, 1115–1124.
- (14) Bradshaw, D.; Garaia, A.; Huo, J. Metal-organic framework growth at functional interfaces: thin films and composites for diverse applications. *Chem. Soc. Rev.* **2012**, *41*, 2344–2381.
- (15) Sarazin, Y.; Howard, R. H.; Hughes, D. L.; Humphreyb, S. M.; Bochmann, M. Titanium, zinc and alkaline-earth metal complexes supported by bulky O,N,N,O-multidentate ligands: syntheses, characterisation and activity in cyclic ester polymerization. *Dalton Trans.* **2006**, *340–350*.
- (16) MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M. Design of supramolecular layers via self-assembly of imidazole and carboxylic acids. *Cryst. Growth Des.* **2001**, *1*, 29–38.
- (17) Chen, C. L.; Su, C. Y.; Cai, Y. P.; Zhang, H. X.; Xu, A. W.; Kang, B. S.; zur Loye, H. C. Multidimensional frameworks assembled from silver(I) coordination polymers containing flexible bis(thioquinolyl) ligands: role of the intra- and intermolecular aromatic stacking interactions. *Inorg. Chem.* **2003**, *42*, 3738–3750.
- (18) Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122.
- (19) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
- (20) Wang, S. H.; Zheng, F. K.; Wu, M. F.; Liu, Z. F.; Chen, J.; Xiao, Y.; Li, R.; Guo, G. C. Assembly of Co(II)/Cu(II)-azidopolynuclear polymers: structural diversity and magnetic behavior. *CrystEngComm.* **2014**, *16*, 2009–2015.
- (21) Gu, Z. G.; Xu, Y. F.; Yin, X. J.; Zhou, X. H.; Zuo, J. L.; You, X. Z. Cluster-based copper(II) coordination polymers with azido bridges and chiral magnets. *Dalton Trans.* **2008**, *5593–5602*.

**Table 1. Bond Lengths (Å) and Bond Angles (°) for 1**

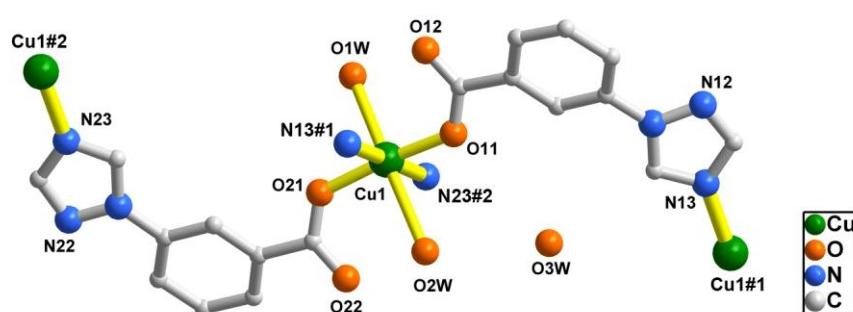
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–O(1W)	2.440(2)	Cu(1)–O(21)	1.9743(19)	Cu(1)–N(13)#2	2.005(2)
Cu(1)–O(11)	1.9495(19)	Cu(1)–N(23)#1	2.002(2)	Cu(1)–O(2W)	2.6470(19)
Angle	(°)	Angle	(°)	Angle	(°)
O(11)–Cu(1)–O(21)	174.68(8)	N(23)#1–Cu(1)–N(13)#2	179.29(8)	N(13)#2–Cu(1)–O(1W)	89.08(9)
O(11)–Cu(1)–N(23)#1	88.55(8)	O(11)–Cu(1)–O(1W)	98.86(8)	N(13)#2–Cu(1)–O(2W)	93.239(58)
O(21)–Cu(1)–N(23)#1	92.23(8)	O(11)–Cu(1)–O(2W)	81.065(56)	N(23)#1–Cu(1)–O(2W)	86.017(57)
O(11)–Cu(1)–N(13)#2	91.27(8)	O(21)–Cu(1)–O(1W)	86.38(8)	O(21)–Cu(1)–O(2W)	93.687(57)
O(21)–Cu(1)–N(13)#2	87.89(8)	N(23)#1–Cu(1)–O(1W)	91.63(8)	O(11)–Cu(1)–O(2W)	81.065(56)
O(1W)–Cu(1)–O(2W)	177.697(52)				

Symmetry transformations used to generate the equivalent atoms: #1:  $x - 1/2, -y + 1/2, z + 1/2$ ; #2:  $x + 1/2, -y + 1/2, z - 1/2$

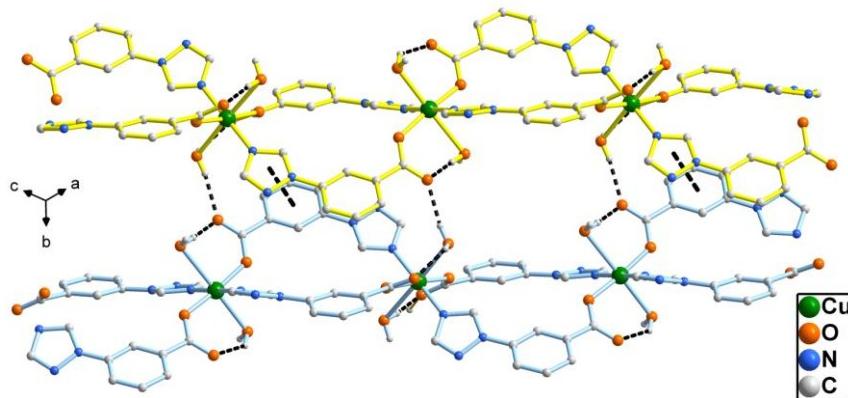
**Table 2. Hydrogen Bonds for Compound 1 (Å and °)**

D–H ·· A	d(D–H)	d(H ·· A)	d(D ·· A)	∠(DHA)
O(1W)–H(1WA) ·· O(12)#1	0.841(17)	2.189(16)	2.881(2)	139.7(19)
O(1W)–H(1WA) ·· O(12)	0.841(17)	2.56(2)	3.171(2)	130.3(18)'
O(1W)–H(1WB) ·· O(22)#4	0.839(18)	2.137(18)	2.974(2)	175(2)
O(2W)–H(2WA) ·· N(12)#3	0.87(2)	2.25(2)	3.111(3)	178(2)
O(2W)–H(2WB) ·· O(22)	0.872(12)	1.842(11)	2.701(2)	168(2)
O(3W)–H(3WA) ·· O(2W)	0.84(3)	2.32(4)	3.107(3)	156(3)
O(3W)–H(3WB) ·· O(1W)#2	0.84(3)	2.48(3)	3.229(3)	149(3)

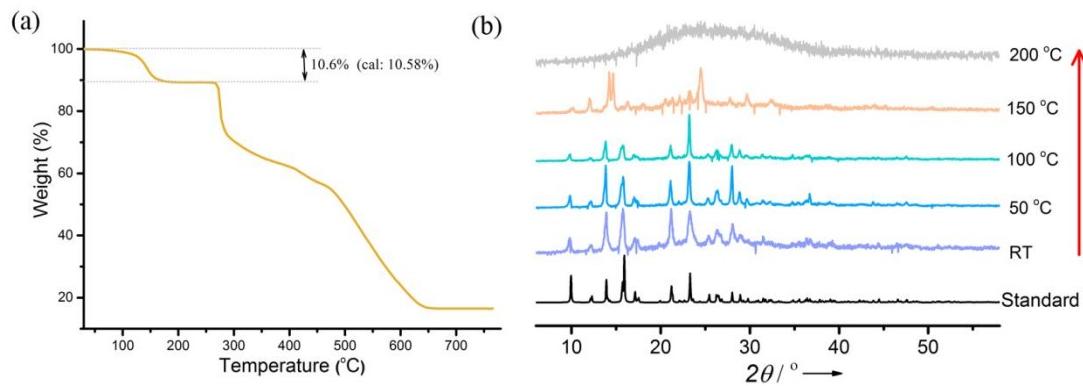
Symmetry transformations used to generate the equivalent atoms: #1:  $1 - x, 1 - y, 2 - z$ ; #2:  $1/2 + x, 1/2 - y, -1/2 + z$ ; #3:  $3/2 - x, -1/2 + y, 3/2 - z$ ; #4:  $1/2 - x, 1/2 + y, 3/2 - z$



**Fig. 1.** Coordination environment around the Cu(II) atoms,  $L^-$  ligand and coordinated water molecules in 1, with hydrogen atoms omitted for clarity. Symmetry codes: #1:  $x - 1/2, -y + 1/2, z + 1/2$ ; #2:  $x + 1/2, -y + 1/2, z - 1/2$

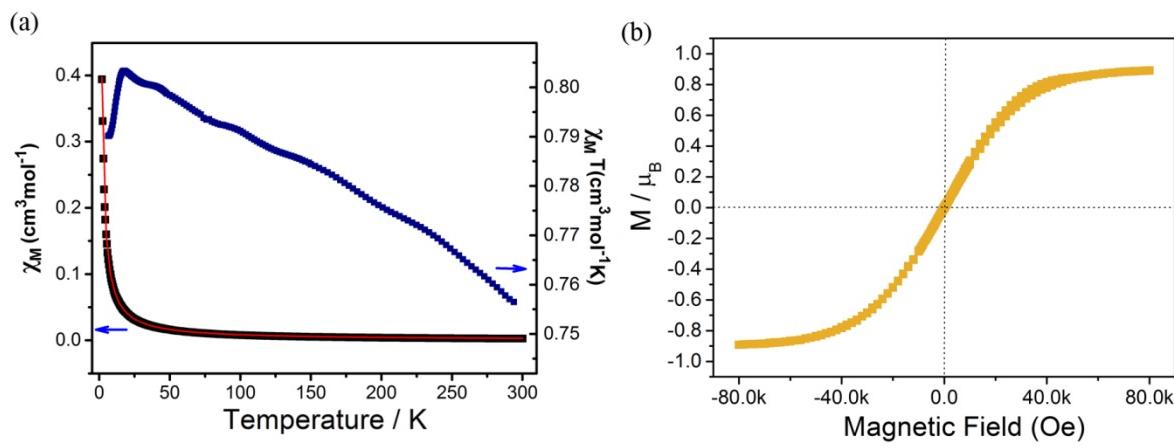


**Fig. 2.** 2D supramolecular structure with the dotted line standing for hydrogen bonds



**Fig. 3.** (a) TGA curve of 1. (b) Comparison of experimental PXRD

patterns for compound 1 to its simulated ones from single-crystal X-ray data

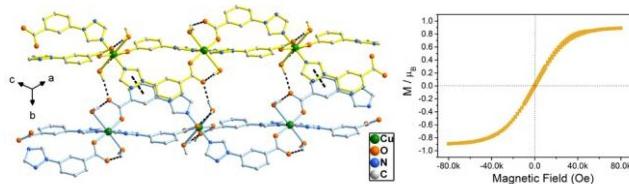


**Fig. 4.** (a) Magnetic susceptibility of 1 plotted as  $\chi_M$  vs. T and  $\chi_{MT}$  vs. T curves, and the

red solid line is the fit to the Curie-Weiss law. (b) Field-dependent magnetization of 1 at 2 K

# A New Copper Coordination Polymer with Magnetic Property Based on 3-(1,2,4-Triazol-1-yl)benzoic Acid

ZHANG Heng-Da(张亨达) WANG Shuai-Hua(王帅华) WU Shao-Fan(吴少凡)



The 2D supramolecular framework is constructed through hydrogen bonding interactions between adjacent 1D chains, in which the [Cu<sub>2</sub>L<sub>2</sub>] clusters connect with each other to fabricate a 1D chained structure, and the magnetic investigation exhibits ferrimagnetic characteristics.